UC Irvine
UC Irvine Previously Published Works

Title
Studies of the correlated electron system SmB6

Permalink
https://escholarship.org/uc/item/0z830860

Journal
Physica B Condensed Matter, 223(1-4)

ISSN
0921-4526

Authors
Kebede, A
Aronson, MC
Buford, CM
et al.

Publication Date
1996-06-01

DOI
10.1016/0921-4526(96)00092-0

Copyright Information
This work is made available under the terms of a Creative Commons Attribution License, availalbe at https://creativecommons.org/licenses/by/4.0/

Peer reviewed

eScholarship.org Powered by the California Digital Library
University of California

ELSEVIER

Physica B 223&224 (1996) 256–259

PHYSICA B

Studies of the correlated electron system SmB_6

A. Kebede[a], M.C. Aronson[b], C.M. Buford[a], P.C. Canfield[c], Jin Hyung Cho[d], B. R. Coles[e], J.C. Cooley[b], J.Y. Coulter[d], Z. Fisk[f], J.D. Goettee[d], W.L. Hults[d], A. Lacerda[d,f], T.D. McLendon[a], P. Tiwari[d], J.L. Smith[d,*]

[a]*Department of Physics, North Carolina A&T State University, Greensboro, NC 27411, USA*
[b]*Department of Physics, University of Michigan, Ann Arbor, MI 48109, USA*
[c]*Ames Laboratory, Iowa State University, Ames, IA 50011, USA*
[d]*Los Alamos National Laboratory, Los Alamos, NM 87545, USA*
[e]*Department of Physics, Imperial College, Prince Consort Road, London SW7 2BZ, UK*
[f]*National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32306, USA*

Abstract

We have prepared high-quality, single crystals of SmB_6 under various conditions to improve sample quality. We have measured the resistivity and magnetic susceptibility from room to liquid-helium temperatures to sort samples. We have applied pulsed magnetic fields as high as 50 T at temperatures as low as 40 mK while measuring resistivity. Our samples are of higher quality than previously known. All solvent-grown, single-crystal samples should be etched to remove a surface conductivity.

1. Introduction

The heavy-fermion materials have properties that are now reasonably well established [1]. The quality of samples of these materials has never been a major issue because the dominance of the heavy electrons over most properties meant that defects and second phases tended not to be noticed. For UPt_3, issues of sample preparation and quality did arise and cloud the symmetry of the superconducting states and the temperature dependence of many properties [2], but in general this has not been a problem. Lately, it has been recognized that a few compounds with "semiconductor-like" ground states should be included in the highly correlated electron materials because the source of the energy gaps at low temperature is not clear and is probably caused by correlation effects [1].

Because a semiconductor-like gap is affected by anything that breaks the translational invariance of the lattice, it seemed useful to improve samples of one of these materials to see if different physics might be revealed. The compound SmB_6 has been studied by condensed-matter physicists for over 25 years and was recognized early as a compound with mixed valence on the samarium atoms [3]. The problem is to distinguish between intrinsic and extrinsic behaviors causing the energy gap. A particular aspect of SmB_6 is that it cannot even have a gap near a half-filled energy band because if the samarium were divalent, the material would be an insulator, and if it were trivalent, it would be half- filled. The samarium is clearly in between these valences, barely having a Fermi sea. Because single crystals of SmB_6 can be prepared in an aluminum solution, there is enormous variation possible in crystal growth conditions, and better crystals could be made. We made many growths of SmB_6, studied crystals by various techniques, and made some preliminary high-magnetic field measurements of resistivity. Most of the measurements were resistive because this tends to make interpretation of the data from a semiconductor view obvious. We simply went looking all around sample and measurement phase space with a Monte Carlo-like approach to see what could be found. We are beginning

* Corresponding author.

0921-4526/96/$15.00 © 1996 Elsevier Science B.V. All rights reserved
PII S0921-4526(96)00092-0

more systematic studies of our samples now because we know what to look for and where. We report here on our preliminary results.

2. Experiments

We prepared 26 useful batches of crystals of SmB_6 by precipitation in molten aluminum. Weighed amounts of samarium, boron, and aluminum were placed in an alumina crucible and heated slowly to 1500°C in a helium atmosphere. Various cooling ramps of up to 200 h were used to cool the solution to the melting point of aluminum 670°C. The crystals were extracted by dissolving the aluminum from them in a warm, concentrated NaOH solution. To optimize the sample quality, in these preparations the Sm to B atomic ratio was varied from 1:4 to 1:8, and the atomic ratio of Sm to Al was varied from 1:17 to 1:393. The purities of the elements used late in the study were Sm – 99.99%, B – 99.5%, and Al – 99.999% to minimize cost while improving samples. The crystals could be etched with dilute HNO_3. We performed modest representative studies of the crystals with X-ray diffraction, with scanning and transmission electron microscopy, and with optical microscopy. Resistance measurements were with four leads and were made with many techniques both AC and DC. Magnetization measurements were made with a Quantum Design Squid System.

3. Results

The quality of SmB_6 samples has been judged by the resistivity increase from room temperature to liquid-helium temperature, called here the resistivity ratio RR [4]. This is certainly a reasonable approach to screening many samples to select the ones with the cleanest energy gaps and is distinct from metals for which the resistivity decreases when cooled. We found that a modest etch of the samples to remove 10–30% of their weight could raise the RR by a factor of at least two up to almost a factor of five. Hereafter all of the results discussed come from etched samples. However, what is more important here is that this result shows that the surface of the single crystals is a conductor that is not representative of SmB_6. What-is-etched-off is shorting out the intrinsic resistance of SmB_6 and causes the resistance to begin to saturate near a temperature of 4 K because its resistance is far below that of pure SmB_6 below 4 K. The removed material has the resistive behavior of a dirty metal; that is, it is temperature independent at low temperature. We were led by this result to fit the resistance of the samples at low

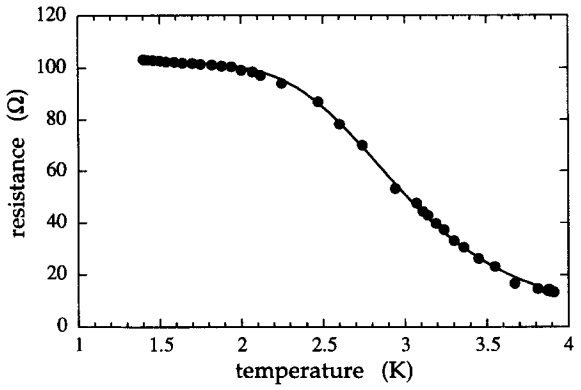

Fig. 1. A fit to the points that show the resistance of SmB_6 as a function of temperature. The smooth line is a fit of a constant resistance in parallel with an activated (energy-gap) resistance.

temperature to a parallel-resistor model. We took the sample to be composed of a constant resistance R_A in parallel with a resistance expressed by $R_B e^{\Delta/2T}$ and show one fit in Fig. 1. Our fits are all very good. For this fit, R_A is 102 Ω, R_B is 0.034 Ω, and Δ is 48.1 K. For this sample, the resistance above about 4 K is thus dominated by the energy gap and shows an exponential behavior, whereas, below about 4 K, the constant series resistance from surface crud dominates the resistance. This is why all reported data show this sort of saturation somewhere near 4 K followed by only a very weak increase in resistance at lower temperatures. We realize that this result modifies the interpretation of previous data taken below 4 K, but this parallel-resistor picture reflects what happens upon surface etching and is more than heuristic. Because the crystal surface is in contact with the aluminum solvent as the aluminum solidifies and cools to room temperature, with different contraction than SmB_6, it is simple to imagine that we do not want to study this surface. This could easily mess up an energy gap of the surface of a material. Our results suggest that the more we etch, the better the sample gets (more activated); so that the surface crud is not a discrete layer but rather is continuously changing spatially.

Because some variation in the RR can be due to extrinsic states in the energy gap, we show in Fig. 2 that, within our scatter, there is no variation of the gap with RR over a large range, as is the case for semiconductors. We have some evidence that the gap does vary as a function of the samarium to boron ratio, which is taken as 1:6 but has a huge variation possible [5]. Our preliminary results (not shown) have a maximum gap energy of 80 K at exactly the ideal ratio to within 0.1 at% variation. The best samples clearly come from batches with the highest ratio of aluminum, that is, very dilute SmB_6.

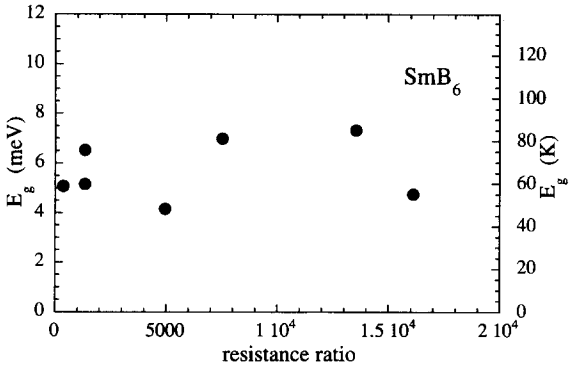

Fig. 2. The energy gap of various samples as a function of the increase in resistance from room temperature to 4 K for each sample.

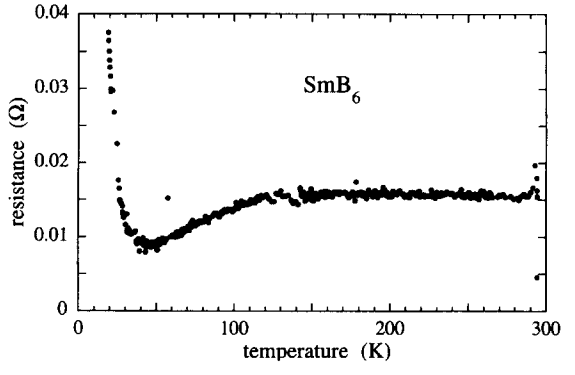

Fig. 3. The resistance of a typical sample plotted to emphasize the maximum near a temperature of 150 K.

Our transmission electron microscopy on ground samples of SmB_6 shows regions of SmB_4 within the samples and occasional edge dislocations within the SmB_6. Our scanning electron microscopy shows many types of defects on the surfaces. Our best samples are relatively free of these, but inclusion of aluminum, edges notched like a comb, and tetrahedral pyramids with their bases parallel to the edges of the crystals all do show up. Our magnetic susceptibility measurements confirm what has been reported for many years [3]. We do notice that bad samples have a distinct and large $1/T$ tail at low temperatures, while better samples show only a monatomic decrease in susceptibility down to our lowest temperature of 5 K. Clearly, samarium that is not at the proper crystallographic sites can be seen magnetically in low-temperature tails. Further work is underway on this measure of sample quality.

Fig. 3 shows a resistance curve plotted to emphasize the maximum near 150 K. Only Lacerda et al. have

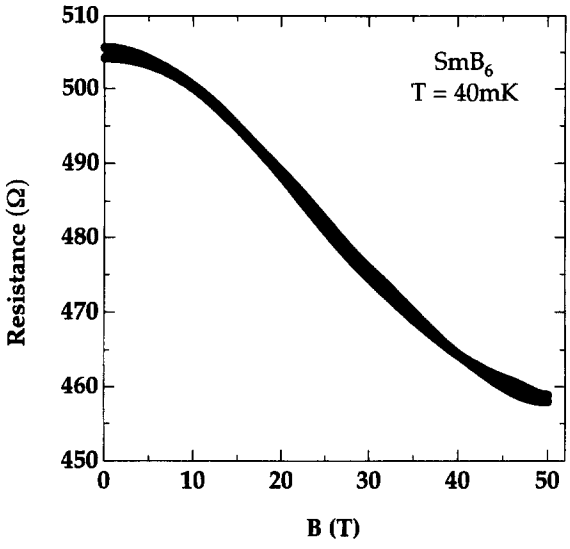

Fig. 4. A very low-temperature resistance trace in a pulsed magnetic field during the full pulse. The closeness of the retrace is indicative that the sample did not heat during the pulse.

reported this before [6]. We see it in all of our better samples, and it might be associated with the "unconventional" magnetic excitation at 13–14 meV seen by neutron scattering [7]. The magnetoresistance of SmB_6 at 40 mK up to a field of 50 T is shown in Fig. 4. To the best of our knowledge, this field and temperature range has not been used before for any published results. Note that the parabolic negative magnetoresistance turns around between 20 and 30 T showing the beginning of saturation. The magnitude of the magnetoresistance is far less than the negative 40% reported at 4 K for the same field range [6]. Our preliminary result at 4 K shows an even larger value at 4 K for the sample used in Fig. 4. Either, the magnetoresistance is indeed decreasing significantly at lower temperatures, which is most unusual, or the data below 4 K are simply measuring the parallel, dirty resistance instead of the SmB_6 behavior, which is seen at 4 K and above, as already discussed.

4. Conclusions

Better samples of SmB_6 have been prepared and measured. The results hold some surprises because the resistive saturation at low temperature is a dirt effect and the activated behavior may hold to the lowest temperature. We note that the resistance maximum near 150 K highlights that this material is not simply a semiconductor at all temperatures. The gap only appears well below room temperature. Some earlier work should be redone with

better samples in order to help understand the cause and properties of the low-temperature, energy gap in SmB_6.

Acknowledgements

This work was supported by the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences; by the US Department of Energy, Office of Defense Programs, Educational Outreach to Historically Black Colleges and Universities Program; and by the National Science Foundation through the National High Magnetic Field Laboratory.

References

[1] Z. Fisk, J.L. Sarrao, J.L. Smith and J.D. Thompson, Proc. Nat. Acad. Sci. USA 92 (1995) 6663; D. W. Hess, P. S. Riseborough and J.L. Smith, Ency. Appl. Phys. (VCH, NY) 7 (1993) 435.

[2] P.J.C. Signore, B. Andraka, M.W. Meisel, S.E. Brown, Z. Fisk, A.L. Giorgi, J.L. Smith, F. Gross-Alltag, E.A. Schuberth and A.A. Menovsky, Phys. Rev. B 52 (1995) 4446; J L. Smith, Philos. Mag. B 65 (1992) 1367; B. G. Demczyk, M. C. Aronson, B. R. Coles and J. L. Smith, Philos. Mag. Lett. 67 (1993) 85.

[3] J.C. Nickerson, R.M. White, K.N. Lee, R. Bachmann, T.H. Geballe and G.W. Hull Jr., Phys. Rev. B 3 (1971) 2030; T. Kasuya, K. Kojima and M. Kasaya, in: Valence Instabilities and Related Narrow-Band Phenomena, ed. R.D. Parks (Plenum, NY, 1977) p. 137.

[4] J.C. Cooley, M.C. Aronson, Z. Fisk and P.C. Canfield, Phys. Rev. Lett. 74 (1995) 1629.

[5] K. Nihara, Bull. Chem. Soc. Japan 44 (1971) 963.

[6] A. Lacerda, D. Rickel, M.F. Hundley, P.C. Canfield, J.D. Thompson, Z. Fisk, P. Haen and F. Lapierre, Physica B 199&200 (1994) 469; A. Lacerda, T. Graf, J.L. Sarrao, D. Mandrus, M.F. Hundley, J.D. Thompson, Z. Fisk and L. Van Bockstal, in: Strongly Correlated Electronic Materials, eds. K.S. Bedell, Z. Wang, D.E. Meltzer, A.V. Balatsky and E. Abrahams, (Addison–Wesley, Reading, MA, 1994) p. 36.

[7] P.A. Alekseev, V.N. Lazukov, R. Osborn, B.D. Rainford, I.P. Sadikov, E.S. Konovalova and Yu. B. Paderno, Europhys. Lett. 23 (1993) 347; J.-M. Mignot, P. A. Alekseev, J. Rossat-Mignod, V.N. Lazukov and I.P. Sadikov, Physica B 199&200 (1994) 430.